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Disclaimer

Ultrafast kinetics subsequent to shock compression in an oxygen-balanced mixture of nitromethane and hydrogen peroxide

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Abstract

We apply ultrafast optical interferometry to measure the Hugoniot of an oxygen-balanced mixture of nitromethane and hydrogen peroxide (NM/HP) and compare with Hugoniot data for pure nitromethane (NM) and a 90% hydrogen peroxide/water mixture (HP), as well as theoretical predictions. We observe a 2.1% percent average deviation between the measured, unreacted Hugoniot of NM/HP and the “universal” liquid Hugoniot based on the measured sound speed at ambient conditions. The data also suggest chemical reactivity near the gas gun initiation threshold of HP and NM in less than ~100 ps post-shock arrival in the sample. This may indicate that, in contrast to HP, chemical initiation in NM/HP is not kinetically limited (on a ~100 ps time scale) between the initiation threshold and the von Neumann pressure.

The propagation of shockwaves in energetic liquids is accompanied by complex physical and chemical phenomena that remain of much interest both experimentally and theoretically[1–3] due to their fundamental and practical relevance. The transition from the shocked but unreacted state to exothermic chemistry is for example yet to be fully understood although it determines important characteristics such as the failure diameter and shock front curvature in detonations[4,5]. The shock behavior of the liquid before the initiation of chemistry is a major component of the modeling efforts to better understand reactivity under shock conditions and has been repeatedly studied experimentally for prototypical liquid explosives like nitromethane[6,7]; more recently molecular dynamics (MD) simulations have also been successfully employed[8,9]. The situation is less satisfactory for most other energetic liquids and particularly liquid mixtures, which remain much less studied despite some recent progress[10]. This is particularly problematic given that most equation of state developments[6,7] and simulations[8,9] rely heavily on experimental data.

Here we report new shockwave measurements on an oxygen balanced mixture of nitromethane and hydrogen peroxide (NM/HP) and compare to unreacted shock Hugoniot data for a 90% hydrogen peroxide/water (HP) mixture (obtained previously[1]), two representative energetic liquids[4,11] with zero and positive oxygen balance, respectively. We also compare the NM/HP data with the empirical liquid Hugoniot proposed by Woolfolk et al.[12], equation of state predictions based on intermolecular interactions[13], and unreacted nitromethane (NM) Hugoniot data from gas gun measurements and our own ultrafast measurements.

The NM/HP sample was a mixture of 90% hydrogen peroxide (in water) and nitromethane with 48.2 (HP)/51.8 (NM) weight fractions. NM and HP are miscible at this concentration.[14] The experimental apparatus is the same as used in previous work[1,15,16], shown schematically in Fig. 1. A chirped ~350 ps duration, ~25 nm full width at half maximum (FWHM) spectral width, 800 nm wavelength pump pulse is focused by a 2 cm focal length lens to ~25 micron FWHM intensity, and drives a shock wave through a ~1 micron thick Al ablator on a glass cover slip into the sample, which is liquid in all cases. Meanwhile, a pair of chirped probe pulses incident from the opposite side measure a time-dependent phase shift (effectively an ultrafast analog to the Velocity Interferometry System for Any Reflector (VISAR)[17] system used in longer time scale experiments) which, via methods described previously[1,15], give the shock speed, the piston speed (ie. the speed of Al/sample interface), and the index of refraction between the shock front and the piston interface. On the probe side, the piston interface is imaged onto the slit of an imaging spectrometer with a 0.28 NA microscope objective, with 10x total magnification between the sample and the detector, and the ultimate spatial resolution is ~2 μm.

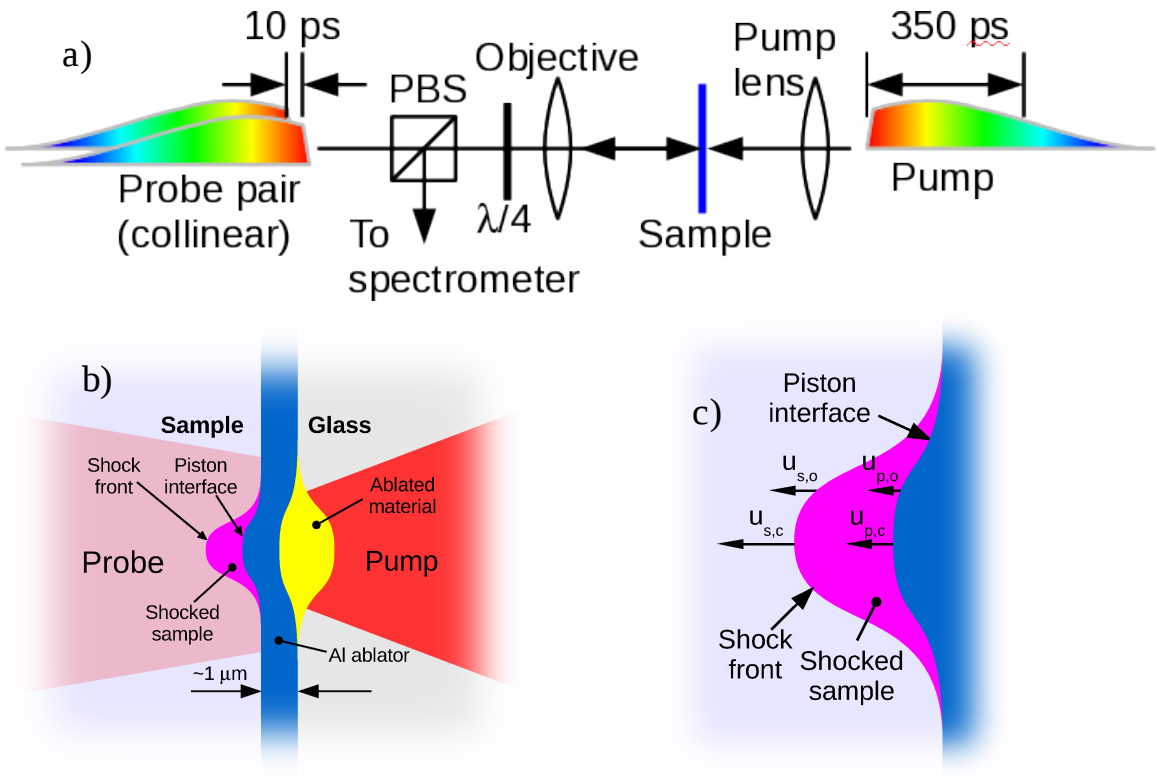

Figure 1: Scheme for shock loading the NM/HP mixture. a) The experimental layout. PBS stands for polarizing beam splitter and λ/4 is a quarter waveplate set to rotate the polarization 90 degrees in double pass. b) A schematic cross section of the experiment at the sample. c) The spatially resolved shock breakout, with the speed of the shock front (u_s) and the piston interface (u_p) at the center of the profile ($u_{s\ or\ p,c}$) and off-center ($u_{s\ or\ p,o}$). Each position in the profile corresponds to a row of pixels (each of which gives an independent time trace) in a CCD at the detector. The horizontal length scale is greatly expanded for clarity – in the actual experiment, off-axis components of velocities are neligible.

This technique obtains a full spatial profile[15,16] of the shock breakout (see Fig. 1c) where the aspect ratio of the experiment is sufficient to assume near 1D compression over the central portion of the profile[16,18]. Since the piston speed varies with spatial position, it is possible (analogous to previous work with UDE[19]) to obtain several points along the Hugoniot simultaneously with a single pump energy. This increases the amount of data which may be obtained per shot, enabling averaging which reduces noise and enables quantitative characterization of the noise in the measurement.

Much previous ultrafast shockwave data is taken from the center of the spatial profile[1,16,20]. For data obtained at multiple pump energies, if shock results from center profile, low energy shots are consistent with off-center results from high energy shots (at constant intensity), the initial assumption of quasi-1D compression, to within error in the experiment, is valid. Also, the effects of a non-constant laser drive profile remain a matter of debate in laser-driven shock experiments, particularly in ultrafast shockwave work. This work does not (and does not intend to) address this issue comprehensively. Yet, we note that, when off-center and center profile results (at different pump energies) obtain the same Hugoniot, the possibility of an explicit pump energy dependence in the measured Hugoniot is excluded; the shock speed is correlated with the corresponding piston speed (which is related to the intensity of the pump at that spatial location[21]), not the pump energy *per se*.

For the NM/HP mixture, we measured shock and piston speeds at three different pulse energies, 41, 50, and 80 μJ. For each pump energy, we obtained between forty and fifty shots. Shock and piston speed pairs were determined for approximately 10 positions near the spatial center of the pump pulse for all shots, and all shots of a given energy and position were averaged to obtain the u_s-u_p data shown in Fig. 2. Error bars are one standard deviation of the data from the mean for data at a given pump energy and spatial position. For pure NM, we obtained center of profile Hugoniot data under conditions similar to HP data obtained previously.[1]

The inset to Fig. 2 shows NM/HP data for 50 μJ pump energy where points along a

spatial 1D cut through the pump profile are labeled by the corresponding position in CCD pixels at the detector. The spacing of CCD pixels scales to 2 μm/pixel at the sample. Consistent with the spatial profile of the pump, the particle speed in the inset to Fig. 2 starts from a minimum on one side of the spatial profile (at pixel 45), reaches a maximum at the center of the pump profile (near pixel 50), and then decreases to another minimum on the other side of the profile (at pixel 55). A similar progression is observed in data at all pump energies.

For a comparison to the universal liquid Hugoniot[12], the sound speed was measured in NM/HP under ambient conditions. The adiabatic speed of sound of the liquid mixture at ambient pressure and 294 K was measured using the impulsive stimulated light scattering technique[22]. A drop of the liquid sample was placed between two borosilicate microscope coverslips separated by a 120 μm thick teflon gasket. The velocity (an average of three measurements) was 1582.0 km/s +/- 1.6 m/s. The acoustic frequency for the measurements was 0.94 GHz; we did not attempt to measure acoustic dispersion as a function of frequency and so cannot be absolutely certain that we measured the fully relaxed sound speed. If a glass-like hydrogen bonding network persists in this mixture then it is conceivable that the sound speed would be approximately 4-8% lower than our measured value.[22] We did not attempt to measure the temperature dependence of the speed of sound (c_0). The change in sound speed with temperature (dc_0/dT) for pure water at ambient pressure and temperature[23] is ~3 m/(s K) and for nitromethane it is –4.3 m/(s K).[6]

For points below 1.7 km/s particle speed, shock speeds are larger than the unreacted universal liquid Hugoniot[12] by an average of 2.1% assuming the measured sound speed (at ambient conditions) of 1.582 km/s, and also larger than a thermochemical calculation of the mixture Hugoniot by 5.1%. The later estimate is based on thermodynamic modeling[13] of the individual mixture components calibrated to available experimental data[1,6,7,13,24]; the difference with the experiments may possibly be due to low temperature mixing effects.

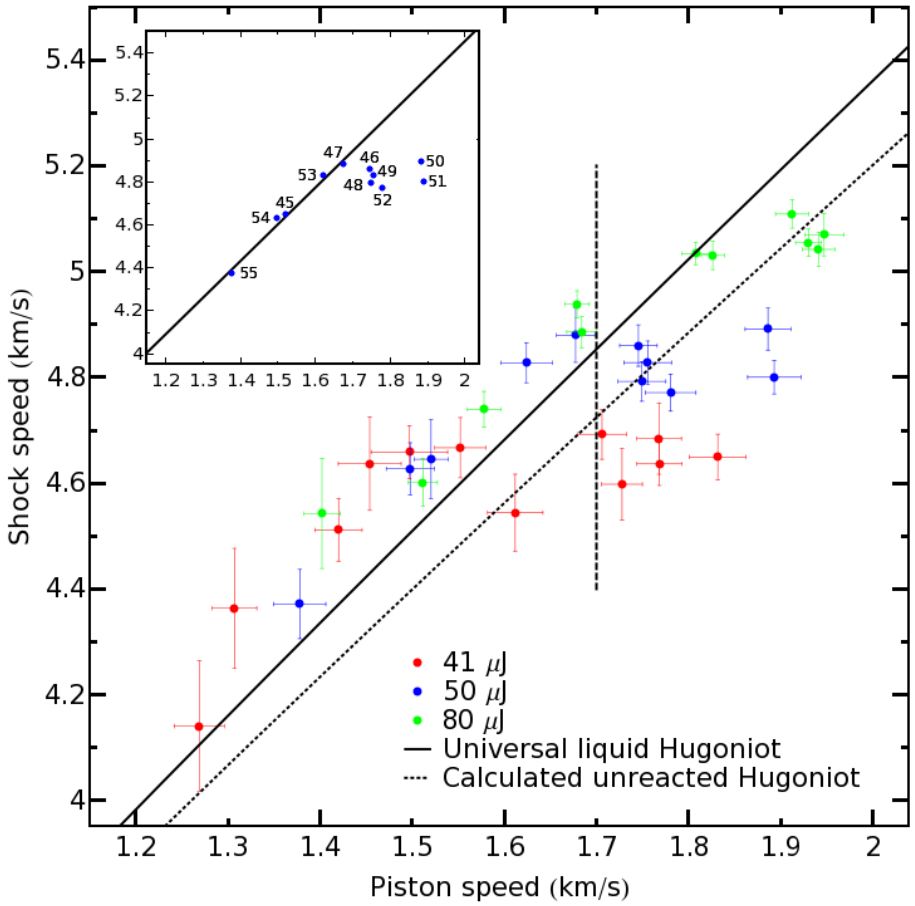

Figure 2: Hugoniot data for the NM/HP mixture, the universal liquid Hugoniot, and the Hugoniot calculated using thermochemical techniques. The vertical dashed line is at 1.7 km/s particle speed, which is near the initiation threshold for HP and NM (see main text). The inset shows the data taken with 50 μJ pump energy (without error bars). Each point is labeled by CCD pixel row, where each pixel row corresponds to a spatial position on the sample along a 1D cut through the pump profile. Pixel 50 is near the center of the profile. A fit to data below 1.7 km/s piston speed is shown as a guide.

Generally, the data below 1.7 km/s piston speed are consistent with a single Hugoniot, independent of pump energy and, as expected, the average piston speed increases with pump energy. Since 1.7 km/s is near the initiation thresholds of both NM (1.84 km/s[25]) and HP (1.7 km/s[26]), henceforth we will refer to data below this value as the unreacted Hugoniot of the NM/HP mixture. Above 1.7 km/s particle speed the data deviate significantly below the extrapolated unreacted Hugoniot, likely due to effects related to

initiation, although the downward trend, possibly indicative of an endothermic effect, is puzzling. This deviation occurs within the 350 ps time window of the experiment, in contrast to previous ultrafast HP data, which do not diverge from the corresponding unreacted Hugoniot for any particle speed between the initiation threshold (of 1.7 km/s particle speed)[26] and the von Neumann pressure for the steady detonation[1]. This may suggest that the initiation mechanism in NM/HP differs from that in HP, with the oxygen-balanced mixture appearing to exhibit significantly faster initial kinetics, perhaps due to its higher energy content.

Ultrafast NM/HP data, NM data compiled from gas gun experiments[25], ultrafast NM data, and ultrafast HP data from previous work[1] are shown in Fig. 3 (all data are included in the supplemental information). The ultrafast HP data were calculated by sorting previously published data[1] by particle speed, and taking an average of every subsequent 5 points in this sorted set. The original HP data set had 100 points distributed in two clusters of 50 points near 1.4 km/s and 2.3 km/s particle speed. The averaged dataset has 20 points total, with the averaged points well-centered in the larger set of unaveraged points. This procedure reduces the scatter per point and makes trends in the data easier to see. The ultrafast NM data were derived from the same averaging procedure applied to center of profile data acquired in the same way as the HP data of ref. 1. Nine averaged points were derived from the original ultrafast NM dataset comprising 45 shots.

Fig. 3c shows the data plotted in the normalized form of Wookfolk et al.[12]. The plot is consistent with the existence of an “universal” liquid Hugoniot (ULH) as proposed by

Woolfolk et al., which posits that all liquid Hugoniot data should fall on the same curve when plotted as $\frac{u_s}{c_0}$ vs. $\frac{u_p}{c_0}$, where c_0 is the speed of sound in the sample under ambient conditions. They suggested the functional form,

$$\frac{u_s}{c_0} = 1 + a\left(-e^{-a\frac{u_p}{c}}\right) + a\frac{u_p}{c_0}, \quad (1)$$

for this "universal" curve, which has the correct limiting behavior at low particle speeds, and trends to a linear dependence at high particle speeds, as usually assumed and often experimentally observed in shock physics; the Woolfolk et al. parameters for the form of eq. 1 are $a_0 = 0.37$, $a_1 = 2$, and $a_2 = 1.62$. Although this relation is the most commonly cited, at least one other form for the high particle speeds liquid Hugoniot was proposed by Voskoboinikov et al.[27], without the exponential term. The Woolfolk et al. ULH matches well the HP and NM/HP data at higher particle speeds ($u_p/c_0 > 1$), with significant deviations occurring for lower values. It is worth noting that there is no fundamental basis for the above functional form (or the ULH idea). For example, we find that the relation,

$$\frac{u_s}{c_0} = 1 + \frac{u_p/c_0}{u_p/c_0 + b_0} - e^{-b\frac{c_0}{u_p}} + \frac{4}{3}\frac{u_p}{c_0}, \quad (2)$$

(shown in Fig. 3c as a blue line), which actually yields the right asymptotic behavior for $u_p/c_0 \to \infty$ (ideal gas limit), works equally well with $b_0 = 0.591$, $b_1 = 4.68$; of course the exponential term can be easily neglected for the particle velocities of interest here. Our fit to the data of Fig. 3c using the form of eq. 1 gives $a_0 = 0.670$, $a_1 = 2.43$, and $a_2 = 1.33$.

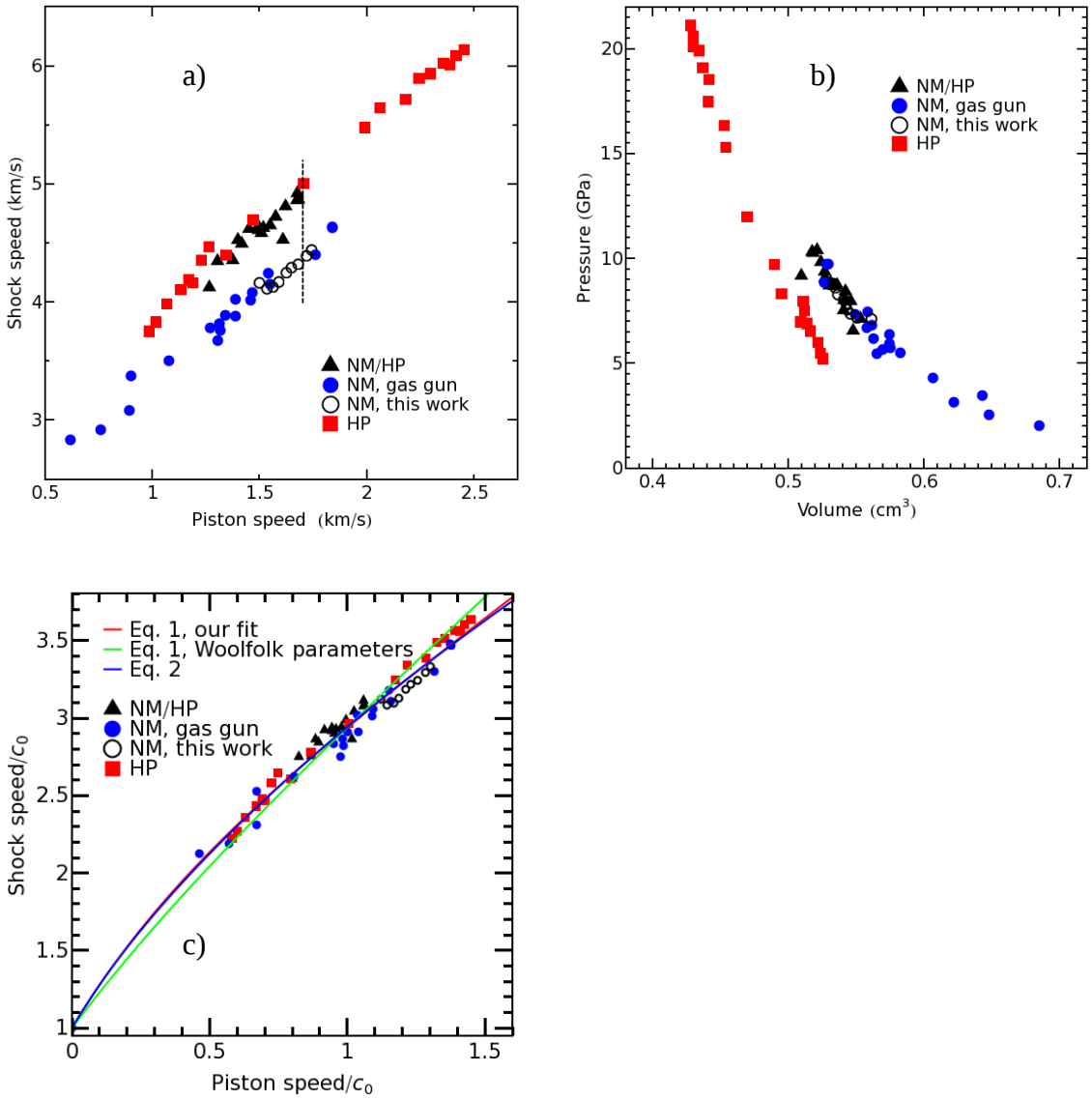

Figure 3: a) Unreacted Hugoniot data for the NM/HP mixture, NM Hugoniot data from previous gas gun experiments, averaged ultrafast NM data, and averaged ultrafast HP Hugoniot data from previous work. The vertical dashed line is at 1.7 km/s particle speed, which is near the initiation threshold for HP and NM. b) Thermodynamic states corresponding to shock data, with initial volumes of 0.79 cm^3 for NM/HP, 0.88 cm^3 for NM, and 0.71 cm^3 for HP. Thermochemical calculations give a temperature for the NM/HP mixture of 920K at a particle speed of 1.7 km/s. c) The same data as Fig. 3a, but in the normalized form of Woolfolk et al.[12], where the shock and particle speeds are normalized by the ambient condition sound speed (for a given sample). The three fits are the Woolfolk form of the ULH[12] (eq. 1) with our fit for the parameters (red), the Woolfolk ULH using his parameters (green), and our form (from the text, blue). The blue and red curves very nearly overlap.

Although unreacted data for all pump energies are consistent with a single Hugoniot for the NM/HP oxygen-balanced mixture, deviations of the data from the unreacted Hugoniot above the 1.7 km/s particle speed 1) depend significantly on the pump energy, and 2) are substantially more scattered than unreacted data. No obvious mechanism explains this, but threshold reactivity effects may play a role above 1.7 km/s particle speed. Future experimental development may enable extending the data to higher particle speeds and longer time scales, and thus help to elucidate these issues.

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